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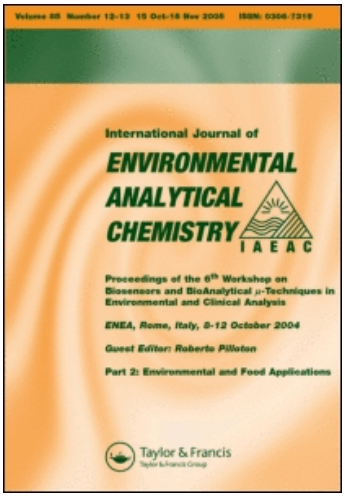

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Evaluation of different calibration approaches in pesticide residues analysis in non-fatty food using fast GC-MS

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Evaluation of different calibration approaches in pesticide residues analysis in non-fatty food using fast GC-MS

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In the analysis of pesticide residues by GC including GC-MS, adverse effects caused by matrix co-extractives occurs which results in worse precision and trueness of analytical results. Sample extracts of various commodities (fruit and vegetables), prepared by the QuEChERS method were evaluated by gravimetric analysis to compare co-extracted compounds amount. For comparison of matrix background measurement of acetonitrile (MeCN) extracts in full scan mode and SIM monitoring were performed utilising fast GC-MS with quadrupole analyser and narrow-bore columns. In order to evaluate the trueness of quantitative analysis results utilising different calibration standards experiments with synthetic samples (it is a blank sample extract from selected fruit and vegetables – apples, pear, cucumbers and cauliflowers, with the addition of pesticides at the concentration level of $0.05\,\mathrm{ng}\,\mu\mathrm{L}^{-1}$ ($50\,\mu\mathrm{g}\,\mathrm{kg}^{-1}$)) were performed in this work. This sample represents a simulated real sample, but with the known concentration to check the various calibration approaches utilising calibration standards that would be used in practice: (1) in organic solvent (MeCN) with addition of analyte protectants (APs), (2) matrix-matched standard, (3) matrix-matched standard with addition of APs. For most of studied pesticides very good match of concentration was obtained utilising matrix matched standards (with/without APs). For the majority of the pesticides under study significant overestimation of concentration was observed in acetonitrile standards with APs in all matrices. Repeatability of measurements expressed as relative standard deviations (RSDs) of determined pesticides concentration in all tested matrices was $\leq 14\%$.

Keywords: fast GC-MS; matrix effects; non-fatty food; calibration; analyte protectants

1. Introduction

Multiresidue methods represent an effective way to screen a large number of samples for multiple pesticides in a relatively short period. However, due to a broad range of physicochemical properties of target analytes within a single analytical run, it can be complicated to obtain low limits of quantification, good precision as well as relevant trueness of results and optimum recoveries for all of them. In addition, the sample matrix can cause an enhancement in the observed chromatographic response for pesticide residues in a matrix extract compared with the same concentration in a matrix-free solution. The matrix can increase the transfer of pesticides from hot vapourising injectors by

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reducing the thermal stress for labile compounds and by masking active sites in the injector responsible for the adsorption or decomposition of polar pesticides. The use of different injector types and matrix simplification procedures can reduce matrix-induced enhancement but do not eliminate it completely [1,2].

There are several approaches in literature to reduce the matrix effect generally. The most reliable and the most expensive approaches to reduction of matrix induced response enhancement are using isotopically labelled internal standards. Their use is rather expensive, especially in a multi-component analysis, where a separate internal standard for each analyte is required [1,3]. The next possibility is the utilisation of totally deactivated GC system, where no active centres are present. But this approach is from a practice point of view not realistic. Generally, the shorter contact time of a sample stream with the injector system, the lower the probability of their adsorption on injector active sites. Significant elimination of adsorption of pesticide residues is achieved using pulsed splitless injection [4], PTV injection [5–9] or direct sample introduction (DSI, DMI) [10–12]. The first option how to reduce/eliminate matrix effects is to perform an efficient clean-up to remove most of the matrix components present in crude extracts. This can be reached by a more selective extraction procedure, or more extensive sample clean-up [13,14]. Solid-phase extraction techniques were well suited to this application, affording extracts with a comparatively low matrix burden, yet several problems persisted in the gas chromatographic analysis of these extracts for pesticide residues. Both the amount and type of matrix affected the perceived recovery [15], and although the general trends remain true, individual pesticides may show different increases in recovery with the same instrumental conditions. Particularly at low residue concentrations, it was not unusual for peak shapes of some pesticides to deteriorate over the course of a sequence of injections interfering in accurate integration of the peaks [1,2,6,16].

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Since an effective elimination of the sources of the matrix induced response enhancement is not likely in practice, analysts often try to compensate for the effect using alternative calibration methods. The most widely used approach in pesticide residue analysis is using matrix-matched standard calibration [1]. This approach also suffers from some drawbacks such as the problems of obtaining a closely matching blank matrix for every sample type, increased instrumentation maintenance, and additional work. In a recent paper [17] the various types of calibrations including matrix-matched standard were tested. Not so often used bracketing calibration in food analysis [6,16,18] based on the calibration of the detection system immediately before and after the analysis of the samples was shown to be advantageous.

The idea to add suitable analyte protectants both to sample extract and calibration standards in organic solvent results in effective equalisation of the matrix-induced response enhancement effect [19,20]. They protect co-injected analytes against degradation, adsorption, or both in the GC system. Various compounds, such as sugars and sugar alcohols, phenolic acids, amino acids, etc. [12,17,19,20] have been evaluated as analyte protectants for improving chromatographic quality of the signal. The advantages of using analyte protectants are simplicity of the procedure, minimisation of analytes losses and thereby significant improvement of peak shapes and lowering detection limits.

The aim of this work was to evaluate different calibration approaches based particularly on matrix-matched standardisation and application of analyte protectants in different non-fatty matrices (apple, pear, cucumber, cauliflower) with addition of selected pesticides to the final extract, and, also, in a real sample extract (apple). The matrices to be evaluated were selected on the basis of their high consumption rate.

Fast GC-MS method with the utilisation of narrow-bore columns, in combination with QuEChERS sample preparation technique [21] was used for analysis. In multiresidual pesticide analysis in order to decrease the matrix effect on the detector site, efficient separation of analytes from the matrix components is important and fast GC with narrow-bore columns is one of the options available [22]. The sample extracts were also subjected to evaluation by gravimetric analysis, to compare the amount of co-extracted sample material and matrix background measurement by fast GC-MS. In our previous work [17], we have already investigated different calibration approaches to fast GC-MS analysis of pesticide residue using APs. Whereas in the present work we are investigating the influence of different matrices with differing amounts of coextractants for a much broader range of pesticides.

2. Experimental

To evaluate suitability of APs to be routinely used in pesticide residues analytical practice, different experiments with testing calibration solutions prepared in different ways and different matrices were carried out. Experiments with solutions of pesticide standards prepared in a neat solvent (MeCN) with APs were performed for better estimation of matrix effects intensity. Experiments with matrix-matched standards were performed for the direct comparison of matrix-matched standardisation with a novel approach – utilisation of APs. Experiments with matrix-matched standards with addition of APs were performed to evaluate the influence of combination of matrix and APs on quality of quantitative analysis, as the combination of both (matrix and APs) might have even stronger effect for analyte responses enhancement. Linearity of responses was studied in the range of concentration from 1 to 500 $ng\,mL^{-1}$ (1–500 $\mu g\,kg^{-1}$ in an original sample) [17].

In order to evaluate the trueness of quantitative analysis results utilising different calibration standards experiments with synthetic samples [17] were performed. Synthetic sample is a blank sample extract from mentioned fruit and vegetables – apples, pear, cucumbers and cauliflowers that were not treated with pesticides, with the addition of pesticides at the concentration level 0.05 $ng\,\mu L^{-1}$ (50 $\mu g\,kg^{-1}$) – a factor five times higher compared to the MRLs (Maximum Residue Level) for baby food (10 $\mu g\,kg^{-1}$). This sample represents a simulated real sample, but with the known concentration to check the various calibration approaches. Pesticides were quantified using different calibration standards prepared at the same concentration level. All experiments were evaluated utilising absolute signals – peak areas and normalised peak areas to two different I.S. – triphenylphosphate (TPP) [12,19,17,20] and heptachlor (HEPT) [1,17,20]. The selection of I.S. was performed according to their application in literature.

2.1 *Reagents and materials*

Standards of pesticides and internal standards (I.S.) were obtained from various sources (Bayer, Leverkusen, Germany; Dr. Ehrensdorfer, Augsburg, Germany; Cheminova, Harboore,Denmark; Ciba-Geigy, Basel, Switzerland; Shering,Kenilworth, NJ, USA; Dow AgroScience, Indianapolis, IN, USA; Agrovita, Ivanka pri Dunaji, Slovak Republic) and were of purity >96%. List of pesticides and I.S. is given in the Table 1. Solution of each from 28 pesticides was prepared in toluene (Merck KGaA, Darmstadt, Germany) at an

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Table 1. List of the used pesticides and internal standards (IS) used, their retention times, monitored ions and SIM group start times.

No.	Compound	Chemical class	Retention time (min)	Monitored ions in SIM, target ion[1]	Group start time in SIM (min)
1	Dichlorvos	Organophosphate	3.69	**185**; 109; 220	3.00
2	Methamidophos	Organophosphate	3.87	**141**; 94; 95	
3	Diphenyl	Aromatic hydrocarbon	4.19	**154**; 152; 153	4.00
4	Acephate	Organophosphate	4.56	**136**; 94; 125	
5	o-Phenylphenol	Phenol	4.76	**170**; 169; 141	
6	Diphenylamine	Aromatic amine	5.18	**168**; 167; 169	5.00
7	Monoctrotophos	Organophosphate	5.52	**192**; 127; 223	
8	Lindane	Organochlorine	5.78	**181**; 11; 219	5.60
9	Pyrimethanil	Anilinopyrimidine	5.91	**198**; 199; 200	
10	Methiocarb	Carbamate	6.52	**168**; 153; 109	6.20
11	Malathion	Organophosphate	6.50	**173**; 127; 158	
12	Cyprodinil	Anilinopyrimidine	6.90	**224**; 225	6.75
13	Methidation	Organophosphate	7.12	**145**; **125**; 302	
14	Myclobutanil	Triazole	7.47	**179**; **245**; 288	7.30
15	Flusilazole	Triazole	7.46	**233**; 315	
16	Cyproconazole	Triazole	7.62	**222**; 224	
17	Trifloxistrobin	Oximinoacetate	7.89	**116**; **186**; 377	
18	Diflufenican	Pyridinecarboxamide	8.13	**266**; 394	8.00
19	Tebuconazole	Triazole	8.18	**125**; **250**; 252	
20	Iprodione	Dicarboximide	8.37	**316**; 216	
21	Phosalone	Organophosphate	8.69	**367**; **182**; 184	8.50
22	Mirex	Organochlorine	8.86	**272**; 274	
23	Pyridaben	Pyridazinones	9.21	**309**; 364	9.00
24	Fluquinconazole	Triazole	9.24	**340**; 341	
25	Etofenprox	Non-ester pyrethroid	9.62	**163**; **181**; 165	
26	Deltametrin	Pyrethroid	10.29	**251**; **181**; 253	10.00
27	Azoxystrobin	Methoxyacrylate	10.41	**344**; 388	
28	Famoxadone	Oxazolidinedione	10.58	**330**; 224	
29	*Heptachlor*	IS	6.32	**272**; **237**; 337	6.20
30	*Triphenylphosphate*	IS	8.16	**326**; 325	

[1]printed in **bold**.

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approximate concentration $1\,mg\,mL^{-1}$. Stock solution of $0.02\,mg\,mL^{-1}$ for all 28 pesticides was prepared in toluene. An internal standard solution of TPP ($1\,mg\,mL^{-1}$) and HEPT ($1\,mg\,mL^{-1}$) was also prepared in toluene. Working standard pesticide mixtures and I.S. solutions with lower concentration were prepared in toluene by dilution. Analyte protectants (APs) which were used for the experiment were: 3-ethoxy-1,2-propanediol (98%), D-sorbitol (99%) and l-gulonic acid γ-lactone (97%) (Aldrich-Chemie GmbH, Steinheim, Germany). Mixture solution of APs was prepared, containing $200\,mg\,mL^{-1}$ of 3-ethoxy-1, 2-propanediol, $20\,mg\,mL^{-1}$ of d-sorbitol, $20\,mg\,mL^{-1}$ l-gulonic acid γ-lactone in acetonitrile (MeCN) (Merck KGaA, Darmstadt, Germany): water (7 : 3), what represents the optimal ratio of APs (10 : 1 : 1) from previous research [12,20]. All stock solutions were stored at $-18^{\circ}C$ and diluted solutions at $+4^{\circ}C$. Standards and analyte protectants were weighed on Sartorius Analytic MC1 scales (Sartorius, Göttingen, Germany). Magnesium sulfate ($MgSO_4$) – clean, anhydrous and sodium chloride (NaCl) – per analysis were from Lachema (Lachema a. s., Brno, Czech Republic).

$MgSO_4$ was annealed at 500°C (5 h) and NaCl at 600°C (6 h). Primary and secondary amine (PSA) sorbent – Bondesil 40 μm was obtained from Varian (Varian Inc., Harbor City, USA).

2.2 *QuEChERS sample preparation method*

Fruit and vegetable (apple, pear, cucumber and cauliflower–non-treated with pesticides; apple, pear and cucumber with peel; cauliflower after removal of outer leaves) were mixed with blender Braun MX 2050 (Braun GmbH, Kronberg, Germany). In the original QuEChERS procedure [21] certain changes were made according to our needs and possibilities [16]: comminution with a chopping device with dry ice was replaced by mixing in a blender, and therefore the homogenisation with Ultra Turrax was used at the extraction step instead of shaking to ensure good extraction efficiencies. Various extraction conditions were tested. Ten grams of each sample weighed into the 50 mL centrifuge tube (polypropylene; Bio-Chrom s.r.o., Bratislava, Slovak Republic) was extracted with 10 mL of MeCN using Ultra-Turrax T 25 basic (IKA Werke GmbH, Staufen, Germany) homogeniser at 19,000 rpm for 3 min. Then liquid–liquid partitioning (LLP) followed: 1 g NaCl and 4 g $MgSO_4$ were added and the mixture was shaken by hand for 1 min. The mixture was then centrifuged (ROTOFIX 32; Hettich centrifugen, Tuttlingen, Germany) at 4,000 rpm (rcf 2701–relative centrifugal force) for 5 min. Portion of the upper layer (7–8 mL) was transferred into a 15 mL centrifuge tube (polypropylene; Bio-Chrom s.r.o., Bratislava, Slovak Republic) containing 25 mg PSA sorbent and 150 mg $MgSO_4$ per 1 mL of the cleaned extract. The mixture was shaken by hand for 1 min, and then centrifuged for 5 min at 4,000 rpm to separate solids from solution. The cleaned extracts (6–7 mL) of the above mentioned fruit and vegetable (blank sample extracts) were used for the preparation of matrix-matched standard solutions and synthetic sample solutions [17] and for the determination of extracts solids.

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2.3 *Determination of extract solids*

Twenty millilitres of the final acetonitrile extract of four different matrices prepared by QuEChERS method was evaporated under N_2, dried at 105°C in laboratory oven until a consistent weight was obtained.

2.4 *Preparation of solutions of synthetic sample*

MeCN standard with APs and matrix-matched standard solutions (for four types of matrix) with and without APs were prepared at a concentration level of 50 ng mL^{-1} corresponding to a pesticide concentration of 50 μg kg^{-1} in a sample. MeCN standard and matrix-matched standard solutions with APs were prepared as follow: 900 μL MeCN/blank sample extract + 25 μL TPP (6000 ng mL^{-1}) + 25 μL HEPT (20 000 ng mL^{-1}) + 25 μL pesticides in toluene (2000 ng mL^{-1}) + 25 μL APs mixture solution. Matrix-matched standard solutions without APs were prepared as follows: 925 μL blank sample extract + 25 μL TPP (6000 ng mL^{-1}) + 25 μL HEPT (20 000 ng mL^{-1}) + 25 μL pesticides in toluene (2000 ng mL^{-1}). The amounts of individual APs injected corresponds to 10, 1 and 1 μg introduced into the GC system using a 2 μL injection. This amounts were found to be the most effective in minimising losses of susceptible analytes and significantly improving their peak shapes (due to reduction of peak tailing) [20].

The synthetic samples were prepared from blank sample extracts with the addition of pesticides at the concentration level 50 ng mL^{-1} (50 μg kg^{-1}) with/without APs, also 2 I.S. were added (prepared the same as matrix-matched standard with/without APs). The order of injections in the sequences was as follows: (A) 1 × MeCN standard solution with APs followed by 1 × synthetic sample with APs for each commodity one after another (apple, pear, cauliflower, cucumber) with 6 repetitions (standard + synthetic sample); (B) 1 × matrix-matched standard solution without APs followed by 1 × synthetic sample without APs for each commodity (as given in A); (C) 1 × matrix-matched standard solution with APs followed by 1 × synthetic sample with APs for each commodity (as given in A). Thus, a total of 48 injections for one type of calibration. For A, B, C calibration sequences 3 × 48 injections were performed. Before each sequence 5 × blank MeCN extract was injected into replaced fresh injector liner and septum for priming the system.

2.5 *Preparation of solutions of real sample*

The apples used in this study as real sample (3 kg, variety Golden Delicius, harvest 2008) were obtained from the farm in South Slovakia, locality Nové Zámky.

MeCN standard with APs and matrix-matched standard solutions with/without APs for real sample were prepared at concentration level of 10 ng mL^{-1} (10 μg kg^{-1}). Two test portions of real sample with/without APs were taken (P1 and P2) and analysed in three GC-MS measurements. The order of the injection in the sequences for real sample utilising bracketing [6,16,18] was as follows: (1–5) extract of clean matrix of apples non-treated with pesticides; (6) MeCN standard solution with APs; (7) P1; (8) P2 (9) MeCN standard solution with APs with the following three repetitions. In the same way the sequences of other matrix-matched standards with APs and matrix-matched standards without APs was carried out.

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2.6 *GC-MS*

GC-MS measurements were performed on an Agilent 6890N GC system coupled to an Agilent 5973 mass-selective detector equipped with a programmed temperature vaporiser (PTV) and an Agilent 7683 autoinjector (2004) and on an Agilent 6890N GC system coupled to an Agilent 5975 mass-selective detector equipped with a PTV (with septum head and liquid CO_2 cryogenic cooling) and an Agilent 7683B autoinjector (2007) (Agilent, Little Falls, DE, USA). MS with electron ionisation (EI) mode (70 eV) was operated in selective ion monitoring (SIM) mode. The used multi-baffled and deactivated PTV liner has the dimensions of I.D. 1.5 mm and volume 150 μL. For each pesticide 2 or 3 specific ions were selected and sorted into groups; the used dwell time was 10 ms per ion. The retention times, target ions, qualifier ions and start times of SIM groups for pesticides and for internal standards are given in Table 1. PTV was operated in solvent vent mode; temperature program for PTV was: 40°C (0.20 min), 400°C min^{-1} to 300°C (2.00 min), 400°C min^{-1} to 350°C (5.00 min). The flow through split-valve was 50 mL min^{-1} and split-valve was closed after 0.2 min and opened after 1.75 min. Chromatographic separation was performed under a temperature program for column: 60°C (1.75 min), 60°C min^{-1} to 150°C, 23.8°C min^{-1} to 300°C (1.90 min). Twenty-eight pesticides and 2 I.S. were analysed in 11.45 min. The total chromatographic run-time, including equilibration before the next injection, was ca 20 min. The injection volume

was 2 μL and after each injection, the syringe was washed with an acetone/water (1 : 1) and followed by MeCN. Helium with purity 5.0 (Linde Technoplyn, Bratislava, Slovak Republic) was used as a carrier gas in constant flow mode 1.2 mL min^{-1} and at the initial oven temperature column headpressure was 234 kPa. Microbore chromatographic column CP-Sil 8 CB (Varian, Middelburg, The Netherlands) with 5% diphenyl 95% dimethylsiloxane stationary phase 15 m × 0.15 mm I.D. × 0.15 μm was utilised. It was connected to a nonpolar deactivated precolumn (1 m × 0.32 mm I.D.) for focusation purposes and better ruggedness of the chromatographic system, via a press-fit connector 0.32–0.2 mm (Agilent Technologies, Basel, Switzerland) and sealed with a polyimide resin (Supelco, Bellefonte, PA, USA).

3. Results and discussion

3.1 *Evaluation of matrices*

As stated before, the matrices evaluated were apple, pear, cauliflower and cucumber. Apple and pear represent fruit of high water content and contents of organic acids, saccharides, peptides, vitamines, glycosides and minerals compounds. Cucumber is a vegetable with high water content too and relatively 'clean' matrix. Contrariwise, cauliflower is vegetable with low water content and more complex matrix (sugars, organic acids, essence).

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Control samples of the selected commodities were evaluated after QuEChERS method with MeCN extraction and dispersive SPE clean-up with PSA sorbent what concerns the weight of co-extractants (extract solids) and matrix background by fast GC-MS measurements utilising analytical narrow-bore column with pre-column (guard column) both in full scan and selective ion monitoring (SIM) mode.

The results of the determination of extract solids show (Table 2), that the weight of matrix components was similar for apple and pear. Extract solids of cauliflower showed higher amount of matrix components and small amount of co-extractants in cucumber compared to fruit extracts. This is in agreement with GC-MS measurements in full scan mode for all the tested matrices (Figure 1, A). Measurements in SIM mode (Figure 1, B) confirm the presence of matrix co-extractants in all tested matrices. The highest burdening of chromatographic system shows cauliflower and the cleanest SIM background offers cucumber acetonitrile matrix.

Table 2. Determination of selected matrices extract solids* for two parallel analyses ($n = 2$).

Matrix	Sample weight (g)	Extract solids (mg)	RSD (%)	Extract solids mg^{-1} 1 g sample
Apple	43.7	20.30	10.2	0.53
Pear	40.4	39.10	1.5	0.48
Cauliflower	41.0	43.30	4.5	1.06
Cucumber	40.2	12.40	8.2	0.31

*MeCN extracts prepared by QuEChERS method were evaporated and dried until a consistent weight was obtained.

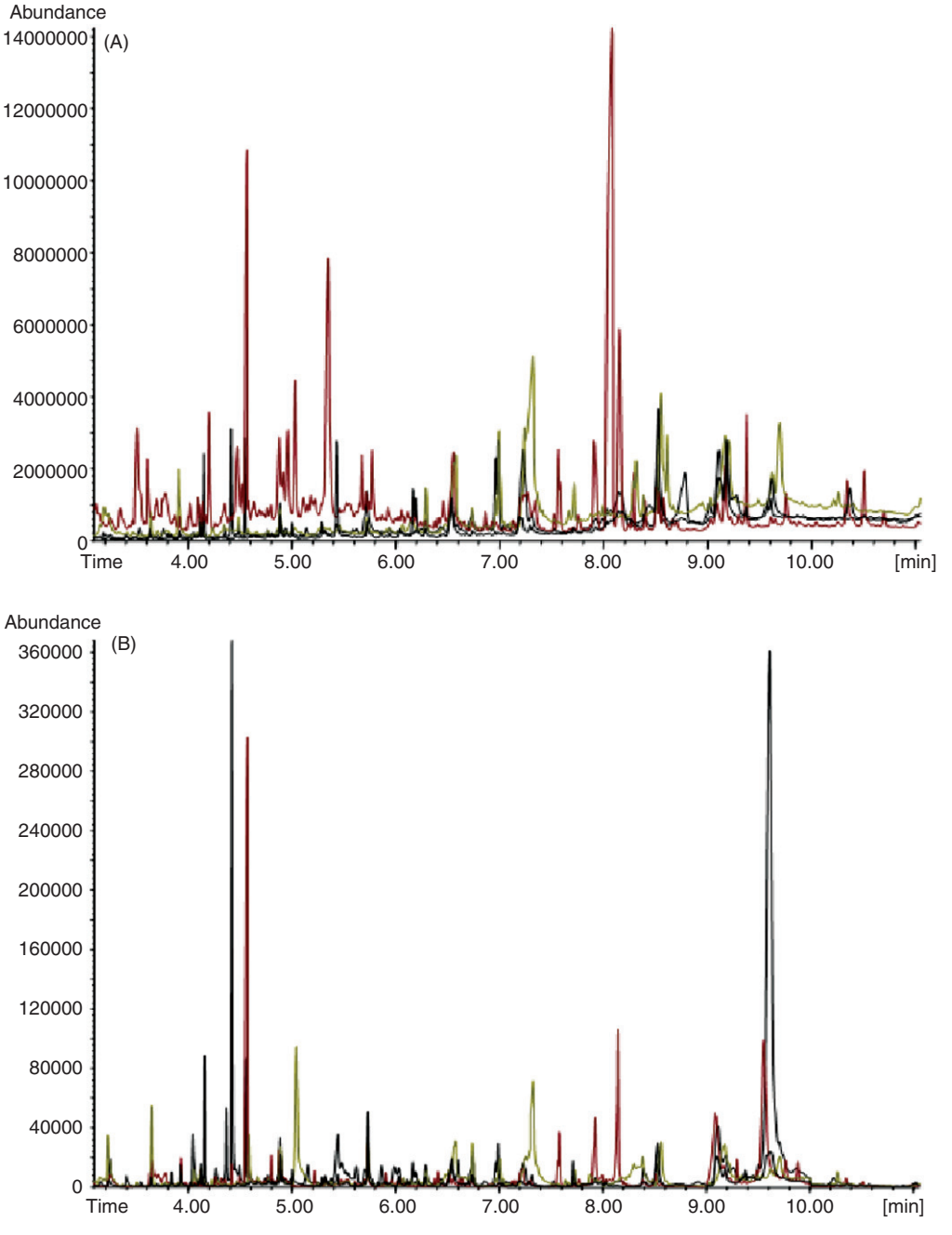

Figure 1. Total ion chromatograms of blank matrix extracts (pear – black line, apple – red line, cauliflower – yellow line, cucumber – green line) analysed by fast GC-MS in: A – fullscan mode (FS), B – selected ion monitoring mode (SIM).

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3.2 *Synthetic sample*

Concentration of pesticides (given in terms of % *vs.* 50 μg kg^{-1}), repeatability expressed as relative standard deviations (RSDs) calculated from absolute peak areas measurements and normalised peak areas and median values (averages of all the % values and RSDs) for apple, pear, cauliflower and cucumber are presented in Tables 3–6, respectively. Low RSDs are obtained for the great majority of compounds for determination of concentration in all calibration approaches (≤10%). Median of RSDs did not exceed 8% in all matrices and approaches studied. The best repeatability was obtained utilising matrix-matched standards without and matrix-matched standards with APs. In Figure 2 chromatograms of extracted target ions of the tested pesticides analysed with fast GC-MS in SIM mode in MeCN standard solutions with APs (A) in comparison with matrix-matched standard solution (B) and matrix-matched standard solution with APs at the concentration 50 ng mL^{-1} (50 μg kg^{-1}) in cauliflower (the most difficult matrix) are presented for illustration. In MeCN standard solutions with the addition of APs there are several unsymmetrical, tailing peaks, whereas in the chromatogram of matrix-matched standards, which have been mostly utilised for the elimination of matrix effects in real practice, the shape of peaks significantly improved. Tailing is minimised when active sites on the stationary phase are being masked by a co-eluting compounds with hight affinity and/or high concentration [21]. Probably, the active sites were physically blocked to analytes access by matrix co-extractants more than in the case of the APs in MeCN standards. For some pesticides the injected amounts of APs might not be sufficient. There are no differences in the peak shape of pesticides in matrix-matched standards with addition of APs compared to matrix-matched standards. It should be pointed out, that measurements were performed in a 'clean' chromatographic system (column and pre-column). Before every type of calibration measurement liner and septa were changed and 5 injections of blank matrix extract was performed, to have similar conditions on the injector site and to avoid adsorption phenomena in a 'dirty' system. The total number of injections performed was 160.

In the case of MeCN standards with APs and quantification using absolute peak areas the overestimation of quantity of a number of pesticides occurs. The overall errors of determination are relatively small except of some pesticides (median < 11% in all matrices). The overestimations observed for the APs may indicate that more APs may have solved the issue, or there could have been a simple bias introduced by the solvent ratio differences (the volume ratio of MeCN/water/toluene was different: matrix-matched standards without APs – 907 μL/18 μL/75 μL; matrix-matched standards with APs – 900 μL/25 μL/75 μL and MeCN standards with APs – 918 μL/7 μL/75 μL). Also, the chosen concentrations for testing is low (50 μg kg^{-1}) with respect to normal amounts injected, which causes greater matrix effects and detection variability than the most common pesticide residues concentrations [23]. The highest overestimation (19–40%) given in terms of % *vs.* 50 μg kg^{-1} obtained from the absolute peak areas was observed for the pesticides pyrimethanil and malathion in all matrices (Tables 3–6). The overestimation >10% obtained from the absolute peak areas was observed for the following compounds in all matrices – o-phenylphenol, methiocarb, tebuconazole, pyridaben and azoxystrobin. The degree of overestimation of results seems to be dependent on the matrix. The maximal value of error of determination of concentration of pesticides obtained from the absolute peak areas was found to be 40% for pyridaben in cucumber matrix and malathion in pear matrix. In some cases also underestimation of quantity was observed. No statistics were

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Table 3. Results of pesticide concentration given in terms of % *vs.* 50 μg kg^{-1} determined in synthetic sample – apple matrix; calculated from absolute peak areas (no I.S.) and normalised areas to TPP (TPP I.S.) and HEPT (HEPT I.S.) using MeCN standards with APs; matrix-matched standards and matrix-matched standards with addition of APs and relative standard deviations (RSD) [%] for six arallel analysis ($n = 6$).

		MeCN + APs			Matrix			Matrix + APs		
		% (RSD)			% (RSD)			% (RSD)		
Pesticide		no I.S.	TPP I.S.	HEPT I.S.	no I.S.	TPP I.S.	HEPT I.S.	no I.S.	TPP I.S.	HEPT I.S.
1	Dichlorvos	106 (3)	86 (9)	88 (7)	96 (6)	102 (6)	100 (8)	99 (8)	95 (7)	98 (10)
2	Methamidophos	100 (4)	86 (3)	89 (3)	102 (3)	109 (4)	106 (4)	83 (8)	78 (8)	81 (10)
3	Diphenyl	116 (2)	100 (1)	100 (4)	106 (5)	113 (6)	109 (4)	100 (1)	99 (2)	103 (2)
4	Acephate	–	–	–	–	–	–	–	–	–
5	o-Phenylphenol	113 (7)	98 (8)	98 (7)	102 (3)	108 (3)	105 (4)	104 (3)	99 (3)	103 (5)
6	Diphenylamine	110 (8)	95 (8)	95 (4)	90 (6)	95 (7)	93 (6)	91 (6)	86 (6)	89 (7)
7	Monocrotophos	–	–	–	–	–	–	–	–	–
8	Lindane	103 (9)	93 (9)	94 (9)	98 (7)	104 (6)	101 (8)	97 (4)	93 (5)	96 (2)
9	Pyrimethanil	119 (3)	102 (4)	103 (6)	103 (2)	109 (2)	106 (4)	101 (5)	96 (5)	100 (6)
10	Methiocarb	122 (6)	105 (7)	105 (6)	97 (2)	103 (2)	100 (4)	100 (4)	99 (8)	102 (7)
11	Malathion	122 (10)	105 (9)	106 (6)	99 (7)	103 (6)	100 (10)	98 (3)	93 (4)	96 (3)
12	Cyprodinil	104 (3)	99 (4)	94 (6)	100 (3)	107 (3)	104 (5)	104 (5)	99 (5)	103 (6)
13	Methidation	110 (9)	95 (9)	95 (8)	96 (1)	102 (2)	99 (4)	99 (2)	95 (1)	99 (5)
14	Myclobutanil	96 (6)	83 (5)	83 (6)	103 (2)	110 (1)	106 (3)	100 (2)	96 (2)	100 (5)
15	Flusilazole	92 (3)	81 (2)	81(4)	101 (1)	107 (2)	104 (3)	102 (3)	97 (4)	101 (3)
16	Cyproconazole	126 (4)	109 (5)	109 (4)	96 (6)	102 (7)	99 (9)	98 (4)	92 (4)	96 (6)
17	Trifloxystrobin	99 (3)	85 (4)	86 (8)	104 (4)	112 (6)	110 (5)	90 (3)	95 (4)	99 (5)
18	Diflufenican	115 (5)	99 (7)	100 (8)	99 (3)	105 (3)	102 (3)	102 (2)	97 (2)	101 (3)
19	Tebuconazole	119 (6)	102 (7)	103 (10)	101 (5)	107 (5)	104 (7)	99 (3)	94 (3)	98 (4)
20	Iprodione	110 (7)	95 (8)	96 (11)	104 (5)	111 (6)	108 (7)	98 (4)	94 (4)	97 (5)
21	Phosalone	132 (8)	117 (10)	117 (6)	98 (4)	105 (5)	102 (6)	103 (2)	98 (3)	102 (5)
22	Mirex	97 4)	84 (3)	84 (4)	102 (2)	109 (2)	106 (5)	103 (2)	98 (2)	102 (4)
23	Pyridaben	123 (4)	106 (5)	107 (8)	103 (4)	110 (5)	107 (6)	101 (2)	97 (2)	100 (5)
24	Fluquinconazole	92 (4)	79 (3)	79 (4)	102 (4)	108 (5)	105 (2)	101 (6)	96 (6)	100 (8)
25	Etofenprox	110 (3)	95 (3)	96 (3)	102 (2)	108 (3)	105 (2)	99 (2)	95 (3)	98 (4)
26	Deltametrin	100 (7)	86 (6)	86 (7)	98 (5)	102 (6)	100 (3)	100 (7)	96 (6)	100 (8)
27	Azoxystrobin	118 (4)	99 (3)	101 (4)	99 (5)	105 (5)	102 (6)	101 (3)	97 (3)	100 (4)
28	Famoxadon	112 (7)	96 (6)	97 (6)	104 (2)	110 (4)	107 (3)	99 (5)	95 (5)	98 (5)
	Median	110 (5)	95 (6)	96 (6)	100 (4)	106 (4)	103 (5)	99 (4)	95 (4)	99 (5)

– means that the pesticide was not detected.

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Table 4. Results of pesticide concentration given in terms of % *vs.* 50 μg kg^{-1} determined in synthetic sample – pear matrix; calculated from absolute peak areas (no I.S.) and normalised areas to TPP (TPP I.S.) and HEPT (HEPT I.S.) using MeCN standards with APs; matrix-matched standards and matrix-matched standards with addition of APs and relative standard deviations (RSD) [%] for six parallel analysis ($n = 6$).

		MeCN + APs			Matrix			Matrix + APs		
		% (RSD)			% (RSD)			% (RSD)		
Pesticide		no I.S.	TPP I.S.	HEPT I.S.	no I.S.	TPP I.S.	HEPT I.S.	no I.S.	TPP I.S.	HEPT I.S.
1	Dichlorvos	102 (8)	82 (10)	86 (8)	94 (4)	83 (6)	95 (8)	99 (4)	97 (5)	92 (7)
2	Methamidophos	104 (6)	99 (9)	103 (4)	108 (2)	97 (1)	108 (6)	99 (6)	97 (6)	92 (7)
3	Diphenyl	108 (5)	86 (8)	90 (5)	104 (4)	92 (5)	106 (4)	99 (2)	97 (2)	92 (5)
4	Acephate	–	–	–	–	–	–	–	–	–
5	o-Phenylphenol	111 (8)	89 (6)	93 (4)	100 (6)	89 (7)	102 (7)	100 (2)	97 (2)	92 (5)
6	Diphenylamine	120 (6)	96 (8)	101 (5)	104 (2)	92 (1)	106 (7)	105 (7)	103 (8)	98 (10)
7	Monocrotophos	–	–	–	–	–	–	–	–	–
8	Lindane	111 (4)	89 (9)	92 (8)	94 (8)	82 (10)	95 (12)	102 (4)	100 (5)	95 (7)
9	Pyrimethanil	131 (8)	105 (10)	110 (7)	105 (2)	93 (2)	108 (8)	102 (3)	99 (3)	94 (4)
10	Methiocarb	116 (6)	93 (6)	98 (9)	103 (6)	91 (6)	105 (10)	107 (5)	110 (12)	104 (13)
11	Malathion	140 (9)	112 (10)	117 (5)	99 (3)	88 (3)	102 (8)	100 (8)	98 (8)	93 (10)
12	Cyprodinil	100 (3)	80 (5)	89 (7)	103 (5)	92 (6)	105 (7)	99 (1)	97 (2)	92 (3)
13	Methidation	135 (6)	108 (6)	113 (8)	113 (5)	102 (5)	117 (8)	109 (5)	110 (6)	104 (8)
14	Myclobutanil	110 (6)	88 (7)	92 (6)	103 (5)	91 (4)	105 (9)	101 (6)	98 (7)	93 (8)
15	Flusilazole	110 (5)	88 (5)	92 (5)	104 (3)	92 (4)	106 (7)	100 (2)	97 (1)	92 (3)
16	Cyproconazole	114 (9)	91 (8)	95 (5)	101 (3)	90 (4)	104 (7)	103 (3)	101 (4)	96 (5)
17	Trifloxystrobin	106 (3)	85 (4)	89 (5)	102 (5)	90 (5)	104 (10)	103 (2)	101 (1)	95 (4)
18	Diflufenican	108 (3)	87 (4)	91 (5)	105 (2)	94 (3)	108 (6)	104 (1)	102 (2)	96 (4)
19	Tebuconazole	116 (5)	93 (3)	97 (4)	96 (6)	83 (7)	95 (10)	101 (1)	99 (2)	94 (4)
20	Iprodione	100 (3)	80 (7)	84 (5)	107 (6)	97 (8)	111 (6)	101 (4)	99 (4)	93 (7)
21	Phosalone	116 (6)	94 (8)	98 (5)	93 (1)	82 (3)	95 (6)	98 (5)	96 (4)	91 (5)
22	Mirex	98 (3)	78 (3)	82 (5)	107 (4)	95 (4)	109 (9)	107 (6)	105 (7)	99 (9)
23	Pyridaben	118 (6)	95 (6)	99 (7)	92 (2)	82 (3)	96 (7)	106 (4)	103 (5)	98 (7)
24	Fluquinconazole	96 (4)	77 (7)	81 (9)	111(3)	98 (3)	113 (7)	84 (4)	82 (3)	78 (3)
25	Etofenprox	104 (2)	83 (7)	87 (5)	104(4)	93 (4)	107 (6)	105 (1)	103 (1)	97 (3)
26	Deltametrin	84 (5)	67 (7)	71 (7)	102(4)	90 (4)	104 (9)	115 (2)	114 (4)	108 (5)
27	Azoxystrobin	127 (7)	102 (6)	106 (4)	102(3)	91 (3)	105 (7)	95 (3)	92 (5)	87 (7)
28	Famoxadon	97 (7)	78 (11)	82 (10)	106(2)	92 (3)	112 (14)	105 (3)	102 (4)	97 (6)
	Median	110 (6)	89 (7)	94 (6)	102 (4)	91 (4)	105 (8)	102 (4)	100 (4)	95 (6)

– means that the pesticide was not detected.

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Table 5. Results of pesticide concentration given in terms of % *vs.* 50 μg kg^{-1} determined in synthetic sample – cauliflower matrix; calculated from absolute peak areas (no I.S.) and normalised areas to TPP (TPP I.S.) and HEPT (HEPT I.S.) using MeCN standards with APs; matrix-matched standards and matrix-matched standards with addition of APs and relative standard deviations (RSD) [%] for six parallel analysis ($n = 6$).

		MeCN + APs			Matrix			Matrix + APs		
		% (RSD)			% (RSD)			% (RSD)		
Pesticide		no I.S.	TPP I.S.	HEPT I.S.	no I.S.	TPP I.S.	HEPT I.S.	no I.S.	TPP I.S.	HEPT I.S.
1	Dichlorvos	107 (11)	82 (6)	81 (3)	103 (3)	97 (2)	101 (2)	111 (5)	105 (5)	110 (8)
2	Methamidophos	–	–	–	106 (4)	100 (5)	104 (5)	94 (6)	87 (7)	91 (10)
3	Diphenyl	121 (4)	93 (6)	93 (9)	107 (3)	101 (2)	105 (2)	99 (3)	93 (4)	98 (7)
4	Acephate	–	–	–	–	–	–	–	–	–
5	o-Phenylphenol	127 (4)	98 (3)	97 (6)	104 (4)	98 (5)	103 (4)	108 (5)	104 (7)	108 (5)
6	Diphenylamine	116 (5)	89 (4)	89 (6)	107 (4)	101 (3)	105 (4)	100 (4)	94 (4)	98 (5)
7	Monocrotophos	–	–	–	–	–	–	–	–	–
8	Lindane	117 (6)	90 (3)	89 (5)	111 (4)	106 (5)	111 (6)	110 (6)	106 (8)	111 (5)
9	Pyrimethanil	139 (6)	107 (5)	107 (9)	104 (1)	98 (2)	103 (2)	104 (3)	87 (3)	102 (6)
10	Methiocarb	121 (5)	92 (9)	91 (13)	93 (9)	85 (10)	84 (9)	99 (6)	93 (6)	97 (7)
11	Malathion	120 (9)	92 (6)	92 (6)	104 (3)	98 (3)	102 (3)	106 (4)	101 (5)	105 (5)
12	Cyprodinil	97 (5)	75 (8)	75 (12)	106 (1)	100 (2)	104 (1)	103 (3)	97 (2)	101 (4)
13	Methidation	109 (13)	84 (9)	83 (8)	102 (5)	96 (6)	100 (6)	104 (7)	100 (8)	104 (11)
14	Myclobutanil	98 (9)	75 (13)	76 (17)	106 (2)	100 (1)	104 (1)	102 (6)	98 (6)	102 (10)
15	Flusilazole	106 (4)	82 (6)	81 (9)	105 (2)	99 (2)	104 (1)	107 (4)	101 (3)	105 (5)
16	Cyproconazole	103 (5)	79 (5)	79 (8)	106 (5)	103 (6)	107 (6)	108 (8)	102 (8)	107 (11)
17	Trifloxystrobin	100 (4)	77 (5)	77 (8)	107 (2)	101 (3)	105 (3)	106 (5)	104 (5)	104 (8)
18	Diflufenican	117 (2)	90 (3)	90 (7)	102 (1)	96 (3)	100 (3)	104 (2)	98 (2)	102 (4)
19	Tebuconazole	112 (4)	84 (6)	85 (10)	105 (6)	99 (4)	103 (5)	105 (3)	99 (3)	103 (4)
20	Iprodione	119(4)	92 (2)	92 (6)	104 (5)	99 (7)	103 (6)	109 (3)	103 (3)	107 (7)
21	Phosalone	108 (8)	83 (6)	83 (6)	99 (4)	93 (4)	97 (3)	99 (5)	93 (5)	97 (7)
22	Mirex	99 (5)	77 (7)	77 (10)	112 (4)	106 (6)	110 (6)	106 (2)	101 (4)	105 (5)
23	Pyridaben	116 (9)	90 (12)	90 (16)	102 (2)	96 (3)	100 (2)	106 (2)	100 (2)	104 (5)
24	Fluquinconazole	88 (4)	68 (6)	67 (9)	99 (5)	93 (3)	97 (4)	105 (2)	98 (2)	103 (5)
25	Etofenprox	109 (5)	84 (2)	84 (5)	107 (2)	101 (2)	105 (2)	102 (2)	96 (2)	100 (5)
26	Deltametrin	88 (7)	68 (8)	67 (10)	109 (4)	104 (4)	109 (4)	125 (6)	119 (7)	124 (6)
27	Azoxystrobin	114 (7)	88 (2)	87 (3)	109 (2)	102 (2)	106 (2)	105 (2)	99 (1)	103 (5)
28	Famoxadon	107 (7)	82 (6)	82 (6)	102 (7)	96 (9)	100 (8)	101 (9)	95 (9)	100 (13)
	Median	110 (6)	85 (6)	85 (8)	109 (4)	103 (4)	107 (4)	109 (5)	103 (5)	108 (7)

– means that the pesticide was not detected.

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Table 6. Results of pesticide concentration given in terms of % *vs.* 50 μg kg^{-1} determined in synthetic sample – cucumber matrix; calculated from absolute peak areas (no I.S.) and normalised areas to TPP (TPP I.S.) and HEPT (HEPT I.S.) using MeCN standards with APs; matrix-matched standards and matrix-matched standards with addition of APs and relative standard deviations (RSD) [%] for six parallel analysis ($n = 6$).

		MeCN + Aps			Matrix			Matrix + APs		
		% (RSD)			% (RSD)			% (RSD)		
Pesticide		no I.S.	TPP I.S.	HEPT I.S.	no I.S.	TPP I.S.	HEPT I.S.	no I.S.	TPP I.S.	HEPT I.S.
1	Dichlorvos	108 (6)	90 (4)	83 (6)	104 (2)	101 (5)	99 (4)	102 (9)	102(9)	104 (12)
2	Methamidophos	–	–	–	107 (3)	103 (4)	101 (5)	94 (10)	94(10)	96 (11)
3	Diphenyl	117 (6)	98 (8)	90 (9)	102 (5)	100 (6)	98 (3)	97 (2)	97(3)	98 (6)
4	Acephate	–	–	–	–	–	–	–	–	–
5	o-phenylphenol	113 (9)	95 (7)	86 (3)	100 (4)	97 (5)	96 (6)	96 (6)	95 (6)	97 (6)
6	Diphenylamine	114 (12)	95 (10)	87 (10)	102 (3)	100 (7)	98 (4)	98 (2)	98 (2)	100 (7)
7	Monocrotophos	–	–	–	–	–	–	–	–	–
8	Lindane	111 (5)	93 (3)	85 (5)	103 (5)	100 (8)	98 (5)	95 (3)	95 (3)	96 (3)
9	Pyrimethanil	131 (7)	110 (6)	100 (6)	100 (4)	97 (6)	95 (4)	100 (4)	100 (4)	101 (7)
10	Methiocarb	114 (7)	95 (6)	87 (10)	99 (5)	96 (9)	95 (8)	104 (6)	104 (6)	106 (8)
11	Malathion	135 (6)	114 (5)	104 (6)	99 (11)	96 (12)	95 (13)	99 (3)	99 (3)	101 (5)
12	Cyprodinil	98 (3)	82 (3)	77 (6)	105 (4)	102 (5)	100 (5)	97 (3)	97 (2)	99 (6)
13	Methidation	123 (12)	102 (9)	103 (5)	101 (6)	98 (7)	96 (8)	103 (7)	100 (8)	102 (11)
14	Myclobutanil	100 (5)	84 (6)	77 (9)	97 (4)	93 (7)	91 (8)	98 (4)	96 (7)	97 (10)
15	Flusilazole	106 (1)	100 (4)	82 (8)	105 (4)	100 (5)	102 (5)	98 (3)	98 (2)	100 (7)
16	Cyproconazole	112 (9)	94 (10)	86 (14)	101 (7)	98 (10)	95 (8)	96 (1)	96 (2)	97 (6)
17	Trifloxystrobin	108 (5)	91 (9)	83 (12)	106 (3)	102 (4)	102 (5)	98 (4)	98 (5)	99 (4)
18	Diflufenican	117 (3)	98 (2)	90 (6)	106 (1)	103 (4)	102 (4)	98 (2)	98 (2)	99 (5)
19	Tebuconazole	116 (5)	98 (8)	90 (10)	103 (3)	100 (3)	99 (3)	106 (6)	106 (6)	108 (9)
20	Iprodione	123 (5)	103 (1)	95 (5)	102 (6)	101 (10)	100 (5)	102 (4)	102 (3)	103 (4)
21	Phosalone	108 (8)	91 (8)	83 (11)	103 (4)	103 (8)	101 (3)	97 (6)	97 (7)	99 (11)
22	Mirex	100 (3)	84 (4)	77 (5)	105 (4)	102 (6)	101 (7)	95 (4)	95 (4)	97 (8)
23	Pyridaben	140 (2)	117 (3)	108 (7)	108 (4)	106 (6)	105 (9)	98 (4)	98 (4)	99 (3)
24	Fluquinconazole	111 (6)	93 (7)	85 (9)	97 (7)	94 (5)	93 (7)	122 (4)	122 (4)	124 (5)
25	Etofenprox	105 (1)	96 (5)	90 (9)	106 (3)	104 (8)	103 (7)	99 (2)	99 (2)	101 (5)
26	Deltametrin	127 (11)	107 (8)	98 (11)	98 (5)	95 (5)	94 (6)	101 (7)	101 (8)	103 (12)
27	Azoxystrobin	122 (8)	102 (4)	93 (6)	98 (3)	96 (7)	94 (8)	107 (2)	107 (3)	108 (6)
28	Famoxadon	126 (9)	105 (8)	96 (8)	103 (4)	100 (8)	98 (4)	100 (2)	100 (3)	102 (6)
	Median	111 (6)	94 (6)	85 (8)	102 (4)	100 (7)	98 (6)	100 (4)	100 (5)	101 (7)

– means that the pesticide was not detected.

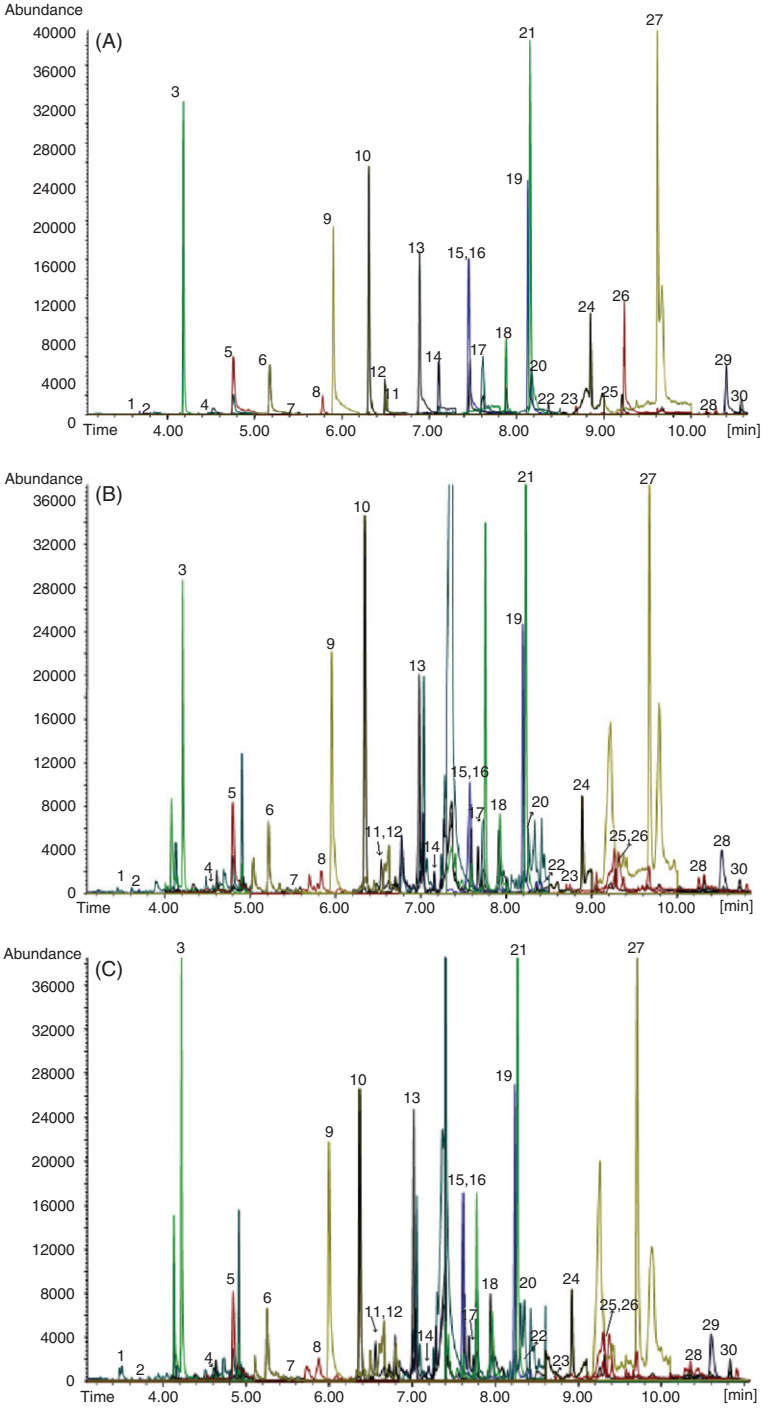

Figure 2. Chromatograms of target ions of 28 pesticides at the concentration level 50 μg kg^{-1} and 2 internal standards (TPP at the concentration level 15 μg kg^{-1} and HPT at the concentration level 50 μg kg^{-1}) analysed by fast GC-MS in: A – MeCN standard solution with APs, B – matrix-matched standard solution without APs (matrix – cauliflower), C – matrix-matched standard solution with APs (matrix – cauliflower). Number of peaks are identical with the number of compounds given in Table 1.

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done to evaluate significance of differences. When quantification utilising TPP is performed, overestimation of troublesome pesticides is slightly lower. Also, TPP and HPT undergoes matrix effects, which can affects the calculation of results with I.S. (the overestimation less when using I.S.). In the case of matrix-matched standards, quantitative data are significantly better for all pesticides under study generally with error of few percent. Similarly good results were obtained also for matrix-matched standards with addition of APs.

The whole study was performed in the 'clean' system. According to our previous study (with 16 pesticides) [17] in a rather 'dirty' system (after 370 injections performed to simulate routine conditions), the overestimation with the use of MeCN + APs standards was higher, up to 60% (for phosalone and deltamethrin). So the degree of overestimation seems to be dependent on the number of injections performed due to fairly small sample capacity of narrow-bore columns [24]. Under these conditions the errors of determination of average concentration utilising matrix-matched standards was only few per cent.

3.3 *Analysis of real sample*

To evaluate performance of APs a real sample of apples with pesticide residues was analysed. The apples used in this study as the real sample were delivered from the farm in South Slovakia. For quantification MeCN standard with APs, matrix-matched standard and matrix-matched standard with addition of APs were used at the concentration level $10\,ng\,mL^{-1}$ ($1\,\mu g\,kg^{-1}$ in original sample). In the real sample four pesticide residues were found: pirimicarb, phosalone, fenarimol and etofenprox. In Table 7 average concentration (average calculated from triplicate analysis of two parallel samples) and relative standard deviations of parallel samples and of GC-MS analyses are given. The determined concentrations of residues were in the range 3–24 $\mu g\,kg^{-1}$. For detected pesticide residues in real sample, RSDs values for parallel samples and for GC-MS are lower than 14%. In Figure 3 chromatogram of extracted target ions of pesticide residues in SIM mode is presented. From the determined pesticides pirimicarb and fenarimol are not in the list of pesticides studied in synthetic sample. The results of phosalone and etofenprox are higher utilising MeCN + APs standards compared to matrix-matched standards, simillary as in the analysis of synthetic sample.

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Table 7. Concentration (c_i) [$\mu g\,kg^{-1}$] of pesticide residues determined in real sample (apples) with different calibration standards and calculation usingabsolute peak areas and repeatability of measurements expressed as RSD [%].

	MeCN + APs			Matrix			Matrix + APs		
Pesticide	c_i	RSD_{PA}[1]	RSD_{GC}[2]	c_i	RSD_{PA}[1]	RSD_{GC}[2]	c_i	RSD_{PA}[1]	RSD_{GC}[2]
Pirimicarb	18	3	5	17	4	4	15	1	3
Phosalone	20	11	6	18	2	6	19	10	5
Fenarimol	4	14	6	4	5	5	4	1	6
Etofenprox	24	2	3	21	4	7	24	3	5

[1] $n = 2$, RSD_{PA} is the relative standard deviation for parallel extraction and analysis of two real sample portions (parallel analysis, PA).
[2] $n = 3$, RSD_{GC} is the relative standard deviation for triplicate GC-MS analysis of one extract of a real sample.

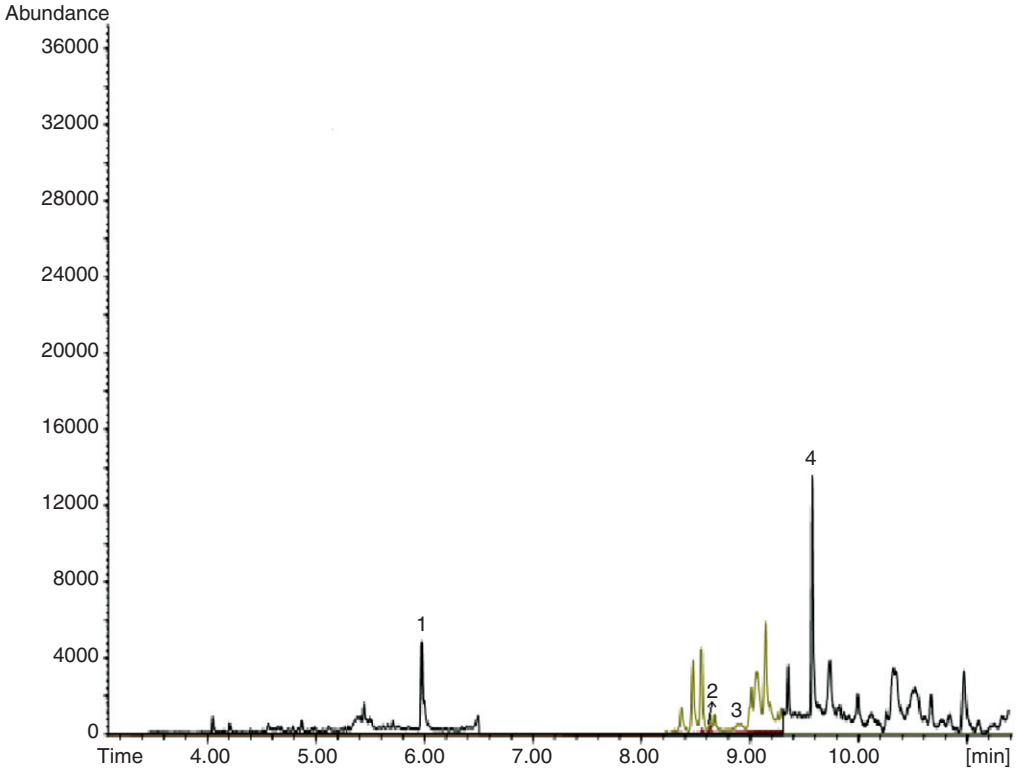

Figure 3. Chromatogram of target ions of pesticides analysed by fast GC-MS in SIM mode in real sample extract. Target ions of pesticides are: 1 – pirimicarb (m/z = 166); 2 – phosalone (m/z = 367); 3 – fenarimol (m/z = 139); 4 – etofenprox (m/z = 163).

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4. Conclusions

Performance of APs as additives for preparation of calibration standards in MeCN and matrix-matched standards was evaluated by comparison with currently widespread used matrix-matched calibration in fruit and vegetables extracts with the set of selected pesticides utilising fast GC-MS with narrow-bore columns and QuEChERS sample preparation method. Sample extracts of fruit and vegetables were subjected to estimation of extract solids to compare amount of co-extracted sample material. For comparison of matrix background measurements of acetonitrile extracts in full scan mode and SIM monitoring were performed. The weight of matrix components was similar for apple and pear. Extract solids of cauliflower showed a higher amount of matrix components and a small amount of co-extractants in cucumber compared to fruit extracts.

The matrix-matched standards with/without the addition of APs provided very similar results of pesticides concentration (given in % *vs.* 50 $\mu g\,kg^{-1}$) in different synthetic samples and was close to the excepted value 50 $\mu g\,kg^{-1}$ with low RSDs. Standards in a neat solvent (MeCN) with the addition of APs yielded overestimation for a number of pesticides under study. The overestimation seems to be matrix dependent and influenced by the number of injections performed. The differences of 3 calibration approaches observed could be considered as low relative to the analytical uncertainties in real-world analyses as shown in

proficiency testing in pesticide residues analysis. The use of APs is the simplest approach. For the routine analytical practice further scientific research with chemometrical tools would be necessary using fast GC with narrow-bore columns.

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